



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

- ¹ Laby, *London, Phil. Mag.*, (Ser. 6), **16**, 1908, (789).
- ² Smith and Menzies, *J. Amer. Chem. Soc.*, **32**, 1910, (1434).
- ³ Smith and Menzies, *Ibid.*, **32**, 1910, (1412).
- ⁴ Pfaundler, *Leipzig, Ann. Physik*, (Ser. 3), **63**, 1897, (36); Morley, *Phil. Mag.*, (Ser. 6), **7**, 1904, (662); Hertz, *Ann. Physik*, (Ser. 3), **17**, 1882, (193); Regnault, *Paris, Mém. Acad. Sci.*, **21**, 1847, (30, 502); **26**, 1862, (506); Ramsay and Young, *J. Chem. Soc.*, **49**, 1886, (37); Young, *Ibid.*, **59**, 1891, (629); Cailletet, Colardeau and Rivière, *Paris, C. R. Acad. Sci.*, **130**, 1900, (1585), etc.
- ⁵ Knudsen, *Ann. Physik*, **28**, 1909, (1002).
- ⁶ Knudsen, *Ibid.*, **29**, 1909, (184).
- ⁷ Knudsen, *Ibid.*, **32**, 1910, (809).
- ⁸ Villiers, *Ann. Chim. Phys.*, (Ser. 8), **30**, 1913, (588).
- ⁹ Haber and Kirschbaum, *Zr. Elektrochemie*, **20**, 1914, (301).
- ¹⁰ Langmuir, *J. Amer. Chem. Soc.*, **35**, 1913, (105).
- ¹¹ Reichsanstalt certificate dated 1914.
- ¹² Menzies, *J. Amer. Chem. Soc.*, probably November, 1919.
- ¹³ Regnault, *Ann. phys. chim.*, (Ser. 3), **15**, 1845, (129); *Mém. Acad. Sci.*, **26**, 1862, (679).
- ¹⁴ Campbell, *Trans. Faraday Soc.*, **10**, 1914, (197).
- ¹⁵ If these two pressures were very close, and if the gauge tubes were too narrow, the total pressure within the hot gauge might be appreciably greater than the pressure within the reservoir.
- ¹⁶ Happel, *Ann. Physik*, (Ser. 4) **13**, 1904, (340), etc.
- ¹⁷ Van Laar, *Verslag. Akad. Wetenschappen*, **24**, 1916, (1635).
- ¹⁸ Van Laar, *Proc. Acad. Sci. Amsterdam*, **20**, 1917, (138).
- ¹⁹ Ariès, *Paris, C. R. Acad. Sci.*, **166**, 1918, (334).
- ²⁰ "A Lower Limit for the Critical Temperature of Mercury," presented before the Division of Inorganic and Physical Chemistry, 1910.
- ²¹ Koenigsberger, *Chem. Ztg.*, **135**, 1912, (1321).
- ²² Menzies, *J. Amer. Chem. Soc.*, **35**, 1913, (1065).
- ²³ Bender, *Physik. Zr.*, **16**, 1915, (246); **19**, 1918, (410).

COHESION, INTERNAL PRESSURE, ADHESION, TENSILE STRENGTH, TENSILE ENERGY, NEGATIVE SURFACE ENERGY, AND MOLECULAR ATTRACTION

BY WILLIAM D. HARKINS

KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO

Communicated by W. A. Noyes, October 14, 1919

Work of adhesion.—For the past seven years I have been engaged in the study of molecular attraction from a new point of view, as represented by a thermodynamic equation which does not seem to have been developed before, in spite of the fact that it is exceedingly simple. It gives what may be called the *total adhesional energy* (E_A), or the total energy involved in the approach of two unlike surfaces. The equation developed by Dupré¹ in 1869 gives the *adhesional work* (W_A), which is

the amount of work involved in the process, which is equal to the decrease of free energy during the approach:

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2} \quad (1)$$

where γ_1 and γ_2 give the free energy of the two unlike surfaces before their approach, and $\gamma_{1,2}$ is the free energy of the interface.

It has been shown by Hardy,² and by Harkins, Brown, and Davies,³ that the adhesional work between organic liquids and water is represented by values which are characteristic for each class of organic compounds. Our own work indicated also that at the interface between water and an organic liquid, any groups in the latter which contain oxygen, nitrogen, or either triple or double bonds, are oriented toward the aqueous phase, while the hydrocarbon radical turns toward the organic liquid. This orientation is of great importance in connection with either the adhesional work or the adhesional energy, since its result is to increase the adhesion between such an organic liquid and water. Further facts which are in accord with this theory of orientation, also developed by Langmuir,⁴ are presented later in this paper, in the section on negative surface energy.

Work of surface cohesion.—Since γ is zero when the two liquids become identical, the Dupré equation reduces to

$$W_{SC} = -\Delta\gamma = 2\gamma \quad (2)$$

where W_{SC} represents the work of the surface cohesion. The free surface energy (γ) is usually measured in ergs per square centimeter. It is evident that W_{SC} is the work necessary to break a bar of liquid or solid with a cross section of 1 sq. cm., in such a way as to give two plane surfaces of 1 sq. cm. each, that is the break must occur perpendicular to the long axis of the bar. This amount of work is clearly that which would be done in the determination of the tensile strength of a steel or other metal bar, if the test could be carried out under *ideal* conditions, which are that the bar during the test must remain of uniform cross section, and the break must occur in such a way as to give two surfaces which are as closely plane as the surface of a liquid, though in the actual tests this condition is not met, since the bar is much distorted. The work of surface cohesion may therefore be called the *tensile work* (W_T). This is equal to the *tensile force* integrated through the distance necessary to pull the two surfaces completely apart, or

$$W_T = \int_{S_0}^{\infty} F_T ds = 2\gamma$$

Energy of adhesion.—The equation developed by me gives the *total adhesional energy* (E_A), and is as follows:

$$E_A = -\Delta E_S = (\gamma_1 + l_1) + (\gamma_2 + l_2) - (\gamma_{1,2} + l_{1,2}) \quad (4)$$

The energy of adhesion is equal to the *total surface attraction*, (π'') due to molecular attraction, integrated through the distance necessary to pull the two surfaces completely apart, or

$$E_A = \int_{S_0}^{\infty} \pi'' ds = E_1 + E_2 - E_{1,2} \quad (5)$$

The only experimental results which have been obtained in connection with equation 4 are those of experiments by Dr. E. C. H. Davies and Mr. Y. C. Cheng as carried out under my direction. This seems to be the first work aside from that on the heat of adsorption, which bears very directly on the molecular attraction between *unlike* substances.

Energy of surface cohesion.—When the two liquids become identical equation 4 reduces to the form

$$E_{SC} = -\Delta E_S = 2(\gamma + l) = 2E_S \quad (6)$$

It is evident that the total energy of surface cohesion is equal to the total tensile energy (E_T), or

$$E_T = -\Delta E_S = 2E_S \quad (7)$$

Thus the *total energy* used in pulling a bar of unit cross section apart in such a way as to form two unit plane surfaces, is equal to twice the total surface energy. It is also equal to the force of surface cohesion (F_{SC}) integrated through the distance necessary to pull the two surfaces completely apart, or

$$E_T = \int_{S_0}^{\infty} F_{SC} ds$$

Energy of cohesion.—The *cohesional energy* of a solid or a liquid may be defined as the energy which would be liberated in the formation of the solid or liquid from its individual molecules, the molecules in the initial state being placed so far apart that they do not attract each other appreciably. This is equal to the latent heat of vaporization plus the heat absorbed in the expansion of the vapor until it becomes very dilute, minus the external work of vaporization, or it is equal to the internal latent heat of vaporization when the liquid is vaporized at a low pressure.

Internal pressure or cohesion.—The internal pressure of a liquid or a solid has been defined as the rate of transfer of momentum across a unit plane area inside the liquid or solid; and the average force of attraction across this unit area, which is numerically equal to the internal pressure, is the cohesive force, or the *cohesion*.

While the work and total energy of adhesion and of surface cohesion, and the energy of cohesion, may all be obtained from experimental results by the use of simple and exact thermodynamic equations, this is not true of the internal pressure or cohesion. As a matter of fact, there is at present no known means of calculating the cohesion, but there are many methods, which do not agree among themselves, of calculating from inexact equations, values which for various liquids are supposed, when arranged in order of magnitude, to lie in the same order in general as the cohesions themselves. In fact, the cohesion is often defined as equal to a/v^2 , the pressure correction term in van der Waals equation. However, since this equation is far from exact in its application to liquids, it is obvious that the cohesion calculated cannot represent at all accurately the internal pressure.

Molecular attraction.—All of the phenomena thus far considered in this paper may be considered as due to the attraction between the molecules in a liquid or a solid. It is customary to consider the molecules as spheres or as points, with the attractive forces dependent upon the distance between the molecules alone, when they are all alike. It has been shown by Harkins, Brown, and Davis,³ by a measurement of the amounts of energy involved, and by Langmuir⁴ by a less direct method, that the forces around different parts of a molecule may be very different in magnitude. Thus in the case of organic compounds the forces are very much higher around any groups containing oxygen, nitrogen, triple, or double bonds, than they are around the hydrocarbon chains. The investigations of Harkins, Grafton and Ewing (these PROCEEDINGS, 5, 1919, 571) show that if organic substances are arranged according to the magnitude of their adhesional surface work toward mercury, they are not so arranged with respect to water. In this respect the adhesional forces seem to have something of the specific nature which indicates chemical action, and it is well known that the recent work on crystal structure demonstrates that such crystals as those of diamond and of graphite are held together by primary valence bonds. Langmuir⁴ considers all cohesive and adhesive forces as chemical, while van Laar⁸ has recently published the results of an extensive series of calculations which show that the square root of van der Waals' con-

stant of attraction (a) is additive, and therefore comes to the conclusion that all such forces are physical. The calculations of Einstein,⁵ Klee-
mann,⁶ and of Harkins and Clark,⁷ have also given coefficients of atomic attraction which are moderately exact constants. Since all of these facts when considered together make it probable that cohesive forces are often less specific than those involved in ordinary chemical reactions, while in many cases they are the same valence forces, it seems to me preferable to use neither of the two words, physical or chemical, and to consider that cohesion is due to electrical and magnetic, or electromagnetic forces, which are probably largely electrical. In a paper^{3c} on "An Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids, and Cohesion" I have already traced a connection between cohesion and the completeness of the outer or valence shell, of electrons in the atom or the molecule. The cohesion decreases as the completeness of the outer shell of electrons in the molecule increases.

On the relation between cohesion and cohesive and adhesive work and energy.—A number of attempts have been made to calculate the cohesion, which is the cohesive force per unit area of the cohesive pressure, from the cohesive surface work, and this attempt has been more or less justified by the fact that the values thus obtained, while not good in numerical agreement with those given by a/v^3 , lie on the whole in the same relative order. Such calculations have been made by Mathews,⁹ and by Hildebrand,¹⁰ but neither of them have shown to what extent the cohesion and the cohesive surface work are related. The term a/v^2 may be said to represent, more or less imperfectly it is true, the total effect of the molecular attraction in decreasing the external pressure, which decrease is the cohesion. The cohesive surface work, on the other hand does not represent the total effect of the molecular attraction, even as it acts in a surface, since the molecules move into the surface not only by means of the energy which is contributed in the form of work, but also by means of the utilization of the kinetic energy of molecular motion, or the latent heat of the surface. Thus the formation of the surface of a pure liquid, with the exception of a few liquids in which liquid crystal formation is involved, is always accompanied by cooling. It is, therefore, the *total cohesive surface energy* and *not the related work*, which represents the total effect of the molecular attraction, or the cohesive effect.

It may seem remarkable, from the point of view of the last paragraph, that the calculation of even the relative cohesion of liquids¹⁰ from a

very simple equation, $\gamma/v^{1/3}$, where V is the molecular volume, should give results which lie in somewhat the correct order. This is undoubtedly because, as shown by Harkins, the contribution of the kinetic energy of a molecule to the total energy of the surface, is on the whole, independent of the nature of the molecule,—at least for such substances as have been used in the calculation of cohesion,—and is dependent on the temperature alone. Therefore, so long as the molecular volume is nearly the same, and the orientation of the molecules in the surface is not an important factor, at any definite temperature the latent heat of the surface is nearly independent of the nature of the substance, so that when substances are arranged in the order of their cohesive surface work or their free surface energy, they are also arranged in the general order of their total surface energy.

A second method of calculating the cohesion from the cohesive work or free surface energy, is based on the well-known assumption of Stefan,¹¹ that the average work involved in bringing a molecule to the surface of a liquid, has one-half of the energy value involved on the average in its complete vaporization. It is obvious from Stefan's paper, that his principle does not involve the *work* but the *total surface energy*, which is supposed to be one-half of the latent heat of vaporization. That this rule is far from true is indicated by the results of extensive calculations by Mr. L. E. Roberts and myself, which show that the fractional contribution of the surface energy toward the complete vaporization increases with the temperature, with a normal range of from one-third at lower temperatures to 0.8 or more as the critical temperature is approached, though the higher values are uncertain. Thus a molecule which at a high corresponding temperature passes from the body of the liquid into the surface, goes, in a *fractional sense with reference to energy*, much more nearly into the vapor state than when the corresponding temperature is low.

Negative surface energy.—The phenomenon of *negative surface energy* was first discovered two years ago by Dr. E. C. H. Davies and me, but has not been announced previous to this time in print. Not only Donnan, but also Tolman and Wolfgang Ostwald, have *assumed* the existence of a negative surface tension or free surface energy. My own investigations have convinced me that the discovery of a negative free surface energy for a plane, uncharged surface is improbable, though it is quite likely that there is such a phenomenon in the case of highly curved phase boundaries. What we have to announce here is the discovery of *a negative total surface energy for a plane, uncharged sur-*

face. Thus, contrary to the rule found in the past, the surface or interface between octyl alcohol and water *gives off energy when it is extended*, but, nevertheless, the *surface cannot be formed without the expenditure of work*. The apparent contradiction is due to the fact that while the molecular motion aids in the formation of an ordinary surface, in the case of the interface under discussion the molecular motion hinders the extension of the surface. This is in accord with the theory presented in our earlier papers, and by Langmuir, that at such an interface there is an orientation of the molecules, since the molecular motion reduces the extent of the orientation.

When the interface between octyl alcohol and water is pulled out adiabatically there is thus a heating of the surface, while an ordinary surface is cooled, so that the potential energy of the molecules is decreased by passing into the alcohol-water interface. The negative surface energy, is, it is true, very small, with a numerical value of two ergs. per sq. cm., while the free surface energy is 8.33, and the latent heat is -10.3 ergs. In contrast with this, it is found that the total surface energy of the hexane-water interface is not only positive but large, with a value of 66.5 ergs. These relations are of considerable interest, and their bearing on interfacial structure, which is of great importance in physiology, will be discussed in a later paper in the *Journal of the American Chemical Society*.

¹ Dupré, *Theorie Mécanique de la Chaleur*, Paris, 1869, p. 69; Lord Rayleigh, *London, Phil. Mag.*, (5) 30, 1890, (461).

² Hardy, *London, Proc. Roy. Soc.*, 86B, 1911, (634).

³ (a). Harkins, Brown, and Davies, *J. Amer. Chem. Soc.*, 39, 1917, (354-64).

(b). Harkins, Davies, and Clark, *ibid.*, 541-96.

(c). Harkins and King, *ibid.*, 41, 970-92, (1919), these PROCEEDINGS, 5, 1919, (152-9).

⁴ Langmuir, *J. Amer. Chem. Soc.*, 39, 1917, (1848-1906), these PROCEEDINGS, 3, 1917, (251-7); abstract in *Met. Chem. Eng.*, 15, 1916, (468). Fraenkel, *Phil. Mag.*, 33, 1917, (297-322).

⁵ Einstein, *Leipzig, Ann. Physik.*, 4, 1901, (513).

⁶ Kleemann, *Phil. Mag.*, 18, 1909, (39, 491, 901).

⁷ Harkins and Clark, unpublished calculations.

⁸ van Laar, *Zs. anorg. Chemie*, 104, 1916, (57-156).

⁹ Mathews, *J. Physic. Chem.*, 17, (603-28).

¹⁰ Hildebrand, *J. Amer. Chem. Soc.*, 41, 1919, (1067-80).

¹¹ *Leipzig, Ann. Physik*, 29, 1886, (655).